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Purification of Gram Quantities of C₆₀. A New Inexpensive and Facile Method.

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Scrivens, W. A.; Bedworth, P. V.; Tour, J. M.

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Department of Chemistry and Biochemistry
University of South Carolina
Columbia, SC 29208

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Purification of Gram Quantities of C₆₀. A New Inexpensive and Facile Method

Walter A. Scrivens, Peter V. Bedworth, and James M. Tour*

Department of Chemistry and Biochemistry

University of South Carolina

Columbia, South Carolina 29208

Abstract

Described is an inexpensive and facile method for the purification of up to gram quantities of C₆₀. The procedure involves the application of a saturated toluene solution of crude fullerenes to a column containing Norit®-A (alkaline decolorizing carbon or activated charcoal) and silica gel (1:2 by weight). Within 37 min, the C₆₀ (purple band) begins to elute from the column and the elution of C₆₀ is nearly complete within 1.2 h to afford 63% yield (of a possible 75% of C₆₀ in extractable fullerenes) with >98% purity.

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Buckminsterfullerene (C_{60}), the newly discovered spherical allotrope of carbon, has precipitated a flurry of recent research endeavors.¹ A severe limitation to this research is the difficulty in producing gram quantities of C_{60} free of the higher molecular weight fullerenes. We describe here a simple and low cost method that uses common laboratory glassware and reagents for the purification of even gram quantities of C_{60} in less than 1.5 h.

Crude fullerene extracts from carbon arc soot contain 70-85% C_{60} and 10-15% C_{70} with the remainder being higher fullerenes.¹ The most common method for purifying crude C_{60} is by column chromatography on activity grade I neutral alumina.² Our experience with this method has shown that to purify 1.9 g of crude fullerenes requires 9.5 kg of alumina, 46 L of solvent, and the procedure takes 16-20 h. About 50% of C_{60} of a possible 75% C_{60} present in the crude can be recovered since activity grade I alumina irreversibly adsorbs some of the C_{60} .² Alumina columns within modified Soxhlet extractors can be used to significantly simplify this method but recovery yields are generally in the range of 33% to 43% out of a possible 75% of C_{60} present.³ Powdered graphite has been used as the stationary phase for chromatographic purification of C_{60} but the recovery of C_{60} is only 32% of a possible 75%.⁴ HPLC has been used for C_{60} purification but it is primarily useful only for small scale separations.^{5,6}

A typical gram-quantity C_{60} purification procedure using our newly developed method is as follows. A slurry of alkaline decolorizing carbon Norit®-A⁷ (36 g) and silica gel⁸ (72 g) in toluene⁹ (200 mL) was poured into a typical glass flash chromatography column (38 mm diameter and 40 cm long) that had a cotton plug at the bottom of the column.¹⁰ The slurry was allowed to settle as the solvent *above* the stationary phase was allowed to drain under a 7.5 psi N_2 head pressure applied at the top of the column.¹¹ The stationary phase must not be allowed to become solvent free or else cracking of the stationary phase can occur. A saturated toluene (400 mL)

solution of crude fullerenes (1.85 g) extracted from carbon arc soot¹² was slowly poured onto the top of the Norit®-A/silica gel stationary phase. A 7.5 psi N₂ head pressure was applied thus providing a ~16 mL/min elution rate.¹³ The deep purple-colored solution containing C₆₀ started to elute from the column after 37 min. After 36 min more, the eluant was nearly colorless and collection of a second fraction was then begun. The total volume of toluene needed for obtaining the C₆₀ fraction (first fraction) was ~600 mL. After 3 min more, a red-brown band characteristic of C₇₀ started to elute. Removal of the solvent from the purple fraction afforded 1.16 g of C₆₀ (63% of a possible 75% of C₆₀ in extractable fullerenes). ¹³C NMR (125 MHz, C₆H₆) analysis of the C₆₀ showed only one peak at δ 143.29 ppm with no other peaks in the spectrum while the signal to noise ratio was 68 : 1.¹⁴ Likewise, mass spectrometric (MS) analysis showed a peak at 720 amu with no detectable peaks for higher molecular weight fullerenes.¹⁵ HPLC on silica gel showed only C₆₀ in the first fraction with no detection of other fullerenes.¹⁶ While the second band eluted from the column was red-brown, it did contain some C₆₀. One more smaller chromatographic run on the initial red-brown portion afforded 74 mg more of C₆₀ and 120 mg of a sample that was 1 : 5 in C₆₀ : C₇₀ as judged by peak height comparison of the MS signals¹⁵ and 1 : 10 in C₆₀ : C₇₀ as judged by HPLC analysis.^{16,17}

Although we illustrated this procedure with 1.85 g of extractable fullerenes, it worked equally well on a smaller scales using the proportionately smaller stationary phases and solvent volumes. Norit®-A alone as the stationary phase without silica gel as a co-phase worked excellently for C₆₀ separations on smaller scales (i.e., 100 mg of crude fullerenes with 2.0 g of Norit®-A); however, the silica gel prevents cracking of the stationary phase in the larger columns and allows for higher flow rates. We also verified the reproducibility of the C₆₀ separations by using Norit®-A from a different distributor (Matheson Coleman & Bell) and the results were nearly identical. Norit®-A/Celite®-521 as a stationary phase is inferior to the Norit®-A/silica gel because with

the former, packing is more difficult and cracking of the stationary phase occurs easily. Molecular sieves (13X) were used as a stationary phase and proved to be inadequate for C₆₀ purifications.

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(7) Alkaline decolorizing carbon Norit®-A was purchased from Fisher Scientific Company.

(8) Flash chromatography grade Silica Gel 60 (230-400 mesh ASTM, 0.040-0.063 particle size) was purchased from EM Science. For the use of silica gel as a stationary phase with activated carbon for the separation of PCBs, see: Sericano, J. L.; El-Husseini, A. M.; Wade, T. L. *Chemosphere* 1991, 23, 915. We thank Professor T. Bidleman for providing us with this reference.

(9) A.C.S. grade toluene was purchased from EM Science.

(10) The design of a typical flash chromatography column can be found in: Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* 1978, 43, 2923.

(11) **CAUTION:** Though we experienced no rupture of the glass under 7.5 - 10 psi pressures, we recommend utilization of this procedure behind a protective transparent shield to prevent injury if a rupture should occur.

(12) We recently developed an apparatus made from common laboratory glassware for the formation of gram quantities (in an 8 h period) of extractable fullerenes from carbon arc soot. The details on the construction of the apparatus will be published shortly.

(13) The stopcock at the bottom of the column can be closed and the pressure slowly released so that more toluene, as needed, can be added. See ref 10.

(14) The parameters used for the ^{13}C NMR analysis were optimized to readily show both C_{60} and C_{70} . A spectrum of the initial crude mixture using the same scanning parameters showed the C_{60} resonance at δ 143.29 (100) ppm and the C_{70} resonances at δ 150.73 (4), 148.18 (11), 147.48 (5), 145.44 (9), and 130.94 (3) ppm. The numbers in parentheses are the relative peak heights.

(15) The mass spectrum was recorded up to 1200 amu. The crude material showed C_{60} at 720 amu and C_{70} at 840 amu in a peak height ratio of 10 : 0.8.

(16) HPLC was done using an Alltech Econosphere silica gel column (250 mm x 4.6 mm I.D.) with 2% toluene in hexane at 1 mL/min using UV detection at 284 nm. The crude material showed a mixture of C_{60} , C_{70} , C_{84} , and possibly other higher fullerenes in a peak area ratio of 58.0, 38.9, 1.6, and 1.5, respectively. The retention times were 5.1, 5.9, 6.6, and 7.4 min, respectively, with baseline separation. Thus, at 284 nm, the extinction coefficient of C_{70} appears to be greater than that of C_{60} therefore skewing detection in favor of C_{70} .

(17) Thus the combined yield of purified C_{60} after two columns was 67% of a possible 75% of C_{60} in extractable fullerenes.